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High-Resolution Angle-Dispersive Powder Diffraction of K(x)Na(1-x)MgF3

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Beamline(s): X3B1

Introduction: The perovskite structure is of the form ABX3. It consists of corner-sharing B-X octahedra that house A cations in 12-fold coordination. Interest in this unique structure stems from a central role in Earth Science: Ferroelastic phase transitions in the perovskite MgSiO3 may explain observed seismic discontinuities in Earth's lower mantle [Shim and Jeanloz 2002]. Multiple industrial applications add interest to perovskite-structured materials, which have found applications ranging from substrates for superconductors [Kawasaki 1999] to electrolytes in solid state fuel cells [Ishihara 1996].

K(x)Na(1-x)MgF3 end member, NaMgF3, is orthorhombic and isostructural to MgSiO3 thus, may be used as a proxy for determining structural behavior at extreme conditions [O'Keeffe 1979]. Two previous studies involving substitution of K for Na in NaMgF3 has reported complete solubility. Phase transitions, first tetragonal (P4/mbm) and then cubic (Pm-3m) where x = ~.35 and x= ~.40 respectively, were also reported [Zhao 1998, Chakhmouradian et. al 2001]. These previous studies have disagreed upon the existence of two-phase regions delineating miscibility gaps within the solid solution. Also, niether study can justify the absence of long-range ordering of A cations at intermediate compositions.

Methods and Materials: The polycrystalline sample of K(x)Na(1-x)MgF3 was prepared in air using conventional solid state methods. High-resolution x-ray powder diffraction patterns were collected at a wavelength of 1.150727 angstroms, making use of a Ge 111 analyzer crystal and commercial NaI scintillation counter. Sample powders were mounted on flat quartz plates and data were collected at compositions where x = (0.0, .15, .30, .35, .40, .45, .50, .55, .60, .70, .80, .90)

Results: X-ray diffraction patterns were input into EXPGUI GSAS and calculated structural models were refined using Rietveld methods to extract precise values of unit cell volumes, atomic positions, K and Na occupancies, and phase fractions. Our data confirms much of the work of Zhao (1998) and Chakhmouradian et. al (2001). We find two-phase regions in the solid solution and raise questions as to the validity of placing sharp phase boundaries at certain potassium occupancies. Analysis suggests the persistence of a secondary tetragonal phase at compositions between 15 and up to 70 mol% K, lending support for a structural model based on short-range octahedral distortion caused by anti-domain boundaries in the orthorhombic (Na rich) and cubic (K rich) regions.

Conclusions: This X-ray analysis will be included in a detailed high-resolution MAS NMR study, which hopes to illuminate the extent of domain boundaries in this system.

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